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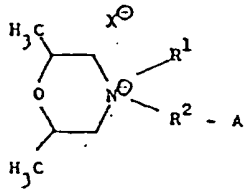
(54) Morpholinio-carbonsäureester- und Morpholinio-alkylphenylethersalze, Verfahren zu ihrer Herstellung und ihre Verwendung als Fungizide.

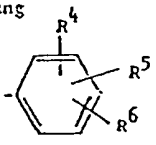
(57) Es werden neue N-Alkyl-2,6-dimethylmorpholinio-carbonsäureester- und N-Alkyl-2,6-dimethylmorpholinio-alkyl-phenylether-Salze der allgemeinen Formel I



(I)

worin A für die Gruppierung

- CO - Z - R^3 oder - O -



steht,

in der R^1 Alkyl mit 6 bis 20 C-Atomen, R^2 Alkylen mit 1 bis 6 C-Atomen, R^3 Alkyl, substituiertes Alkyl, Alkenyl, Alkinyl, Cycloalkyl, substituiertes Cycloalkyl, Cycloalkylalkyl, Aryl, substituiertes Aryl, Aryl-nieder-alkyl, substituiertes Aryl-nieder-alkyl, Z Sauerstoff oder Schwefel R^4, R^5 und R^6 unabhängig voneinander gleich oder verschieden Wasserstoff, Alkyl, Alkoxy, Acyl, Halogen, Halogen-alkyl, Cycloalkyl, Aryl-nieder-alkyl, Aryl, Nitro, Cyano, Thiocyanato, NHCOR', COOR' und/oder CONR'R'' und X^- das Anion einer Säure bedeuten, Verfahren zu ihrer Herstellung und ihre Verwendung als Fungizide zur Bekämpfung von pilzlichen Schaderregern in der Landwirtschaft und im Gartenbau beschrieben. Zusätzlich besitzen diese Verbindungen auch pflanzenwachstumsregulierende Eigenschaften.

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Croydon Printing Company Ltd

Morpholiniocarboxylic ester salts and morpholinio alkylphenyl ether salts, methods of producing them and their use as fungicides

The invention relates to novel N-alkyl-2,6-dimethylmorpholiniocarboxylic ester salts and N-alkyl-2,6-dimethylmorpholinio alkylphenyl ether salts, to their preparation and to their use as fungicidal agents in agriculture and horticulture with additional plant-growth-regulatory properties.

It is known to use N-alkylmorpholines and their salts as well as their molecular compounds and addition compounds as fungicides (DE-PS 1 164 152, DE-PS 1 173 722, DE-PS 24 61 513).
It is furthermore known that quaternary ammonium compounds of long-chain N-alkyl-2,6-dimethylmorpholines having lower alkyl, alkenyl, alkoxyalkyl or aralkyl substituents are fungicidally active (DE-PS 1 167 588; Angewandte Chemie 77 (1965), p. 327-333). There are furthermore known compositions which contain substituted N-benzyl- or alkoxymethyl-2,6-dimethyl-morpholinium salts as active compounds for combating fungal pathogens (DD 134 037, DD 134 474, DD 140 403). It is furthermore known that salts of morpholinocarboxylic esters with long-chain alkanesulphonic acids or alkanecarboxylic acids have fungicidal properties (DD 201 371).

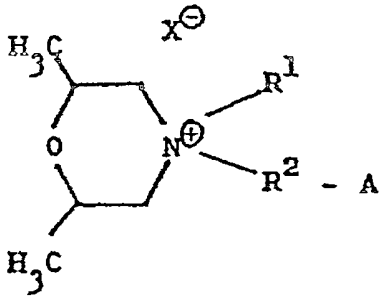
It is furthermore known that morpholinoalkyl alkyl ethers, 4-alkylcyclohexyl ethers and 4-alkylaryl ethers have fungicidal properties (DE-PS 1 190 724; Angewandte Chemie 77 (1965), p. 327-333; Angewandte Chemie 92 (1980), p. 176-181). It is furthermore already known to use 2,3-dihydro-6-methyl-5-phenylcarbamoyl-1,4-oxathiine 4,4-dioxide (oxycarboxin), N,N'-bis(1-formamido-2,2,2-trichloroethylpiperazine (triforine) or zinc ethylenebisdithiocarbamate (zineb) as active compounds in fungicidal compositions for combating

fungal plant diseases (The Pesticide Manual, British Crop Protection Council; London, 1984).

However, the activity of the above-mentioned compounds in certain fields of indication is not always fully satisfactory, in particular when low rates and concentrations are applied. Moreover, they have a fairly high selectivity regarding certain species of fungal pathogens, which greatly limits the broad use of these compositions. A further disadvantage is that the plant tolerance of these compounds is not sufficient in many cases.

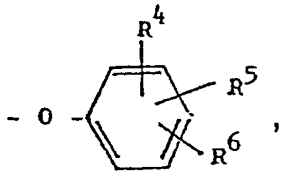
The invention is based on the object of providing novel N-alkyldimethylmorpholiniocarboxylic ester salts and fungicidal compositions containing them which have a good activity and a broad spectrum of action and as high as possible a plant tolerance and additional plant-growth-regulatory properties.

To achieve this object there are proposed compounds which are characterized in that they contain at least one N-alkyl-2,6-dimethylmorpholiniocarboxylic ester salt or N-alkyl-2,6-dimethylmorpholinio alkylphenyl ether salt of the general formula I,



(I),

wherein A represents the group

$-CO-Z-R^3$ or  ,

in which

R^1 represents straight-chain or branched alkyl having 6 to 20 C atoms,

R^2 represents straight-chain or branched alkylene having 1 to 6 C atoms,

R^3 represents straight-chain or branched alkyl having 1 to 20 C atoms,

a straight-chain or branched alkyl which has 1 to 6 C atoms and which is substituted by halogen, hydroxyl, alkoxy having 1 to 4 C atoms, dialkylamino having 2 to 16 C atoms, nitro and/or cyano,

an alkenyl which has 2 to 6 C atoms and which is optionally substituted by halogen,

alkynyl having 3 to 6 C atoms,

cycloalkyl having 3 to 12 carbon atoms, it being possible for the cycloalkyl radical optionally to be substituted by one or more alkyl radicals having 1 to 7 C atoms,

cycloalkylalkyl having 4 to 10 C atoms,

aryl which can be monosubstituted or polysubstituted by identical or different substituents from the series consisting of straight-chain or branched alkyl having 1 to 6 C atoms, alkoxy having 1 to 4 C atoms, aryl-lower-alkyl having 7 to 12 C atoms, acyl having 1 to 4 C atoms, halogen, aryl, nitro and/or cyano,

aryl-lower-alkyl which has 7 to 12 C atoms and which can be monosubstituted or polysubstituted by identical or different substituents from the series consisting of straight-chain or branched alkyl having 1 to 6 C atoms, alkoxy having 1 to 4

C atoms, halogen, haloalkyl having 1 to 4 C atoms, nitro and/or cyano,

R^4, R^5 and R^6 independently of one another represent identical or different substituents from the series consisting of hydrogen, straight-chain or branched alkyl having 1 to 6 C atoms, alkoxy having 1 to 4 C atoms, acyl having 1 to 4 C atoms, halogen, haloalkyl having 1 to 4 C atoms, cycloalkyl having 3 to 7 C atoms, aryl-lower-alkyl having 7 to 12 C atoms, aryl, nitro, cyano, thiocyanato, NHCOR', COOR' and/or CONR'R" it being possible for R' and R" independently of one another to represent hydrogen, straight-chain or branched alkyl having 1 to 6 C atoms, aryl or aryl-lower-alkyl having 7 to 12 C atoms,

Z represents oxygen or sulphur and

$X^{\ominus}$ represents the anion of a nonphytotoxic acid,

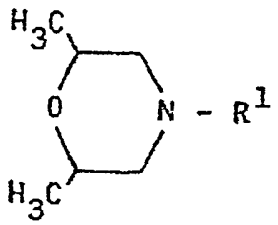
in addition to the customary solvents, carriers and/or formulation auxiliaries.

The compounds according to the invention can exist in two different geometric structures as N-alkyl-2,6-cis-dimethylmorpholiniocarboxylic ester salt and N-alkyl-2,6-cis-dimethylmorpholinio alkylphenyl ether salt or N-alkyl-2,6-trans-dimethylmorpholinio-carboxylic ester salt and N-alkyl-2,6-trans-dimethylmorpholinio alkylphenyl ether salt or as the respective mixtures of these two isomers. Not only the isomer mixture as is generated by the synthesis, but also the individual isomers, can be used for the fungicidal application.

Surprisingly, it has been found that the N-alkyl-2,6-dimethylmorpholiniocarboxylic ester salts and N-alkyl-2,6-dimethylmorpholinio alkylphenyl ether salts of the general formula I according to the invention have a potent fungicidal activity and a broad spectrum of action and are suitable in particular for combating phytopathogenic fungi on crop plants and on stored plant-based products. The active compounds are well

tolerated at the application rates required for the combat of plant diseases. In addition, the compounds according to the invention can have a desired positive effect on crop plants, given their growth-regulatory properties.

The N-alkyl-2,6-dimethylmorpholiniocarboxylic ester salts and N-alkyl-2,6-dimethylmorpholinio alkylphenyl ether salts of the general formula I are obtained by reacting an N-alkyl-2,6-dimethylmorpholine of the formula II,

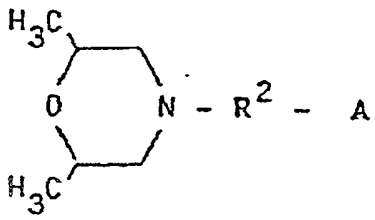


(II)

wherein R^1 has the meaning given in the general formula I
with a compound of the formula III

$$X - R^2 - A \qquad \text{(III)}$$

wherein R^2 and A have the meaning given in the general formula I and X represents halogen,
or, alternatively, reacting a 2,6-dimethylmorpholino-carboxylic ester or 2,6-dimethymorpholino alkylphenyl ether of the formula IV,



(IV)

wherein R^2 and A have the meaning given in the general formula I
with a compound of the formula V,

$$R^1 - X \qquad (V)$$

wherein R^1 has the meaning given in the general formula I and X represents halogen.

N-alkyl-2,6-dimethylmorpholines of the formula II are, for example, n-decyl-, n-dodecyl-, n-tridecyl-, iso-tridecyl-, 1,5,9-trimethyldecyl-, n-pentadecyl- or n-didecyl-2,6-dimethylmorpholine.

Halocarboxylic esters of the formula III are, for example, C_1-C_{20}-alkyl chloroacetate, 4-chlorobutyl chloroacetate, 4-hydroxybutyl chloroacetate, 2-ethoxy-ethyl chloroacetate, 2-cyanoethyl chloroacetate, 2-nitroethyl chloroacetate, cyclohexyl chloroacetate, methyl 2-bromopropionate, allyl 2-bromopropionate, 1-naphthyl 2-bromopropionate, phenyl chloroacetate, phenyl thiochloroacetate, methyl 2-bromobutyrate, benzyl 2-bromocaproate, 4-chlorophenyl chloroacetate, 4-tert-butylphenyl chloroacetate, 3,4-dichlorophenyl chloroacetate, 2,6-dimethylphenyl chloroacetate, 2,6-dibromo-4-nitrophenyl chloroacetate, 2,6-dibromo-4-cyanophenyl chloroacetate, 2,6-dichlorobenzyl chloroacetate, 4-cyanobenzyl chloroacetate, 4-nitro-phenyl chloroacetate or the chloroacetate anion.

Haloalkylphenyl ethers of the formula III are, for example, 2-bromoethyl phenyl ether, 2-chloroethyl-4-tert-butyl phenyl ether, 2-bromoethyl 4-nitrophenyl ether, 2-bromoethyl 4-cyanophenyl ether, 2-bromoethyl 2,6-dichlorophenyl ether, 2-bromoethyl 3,4-dichlorophenyl ether, 2-bromoethyl 2,6-dichloro-4-cyanophenyl ether, 2-bromoethyl 3,5-dichlorophenyl ether, 2-bromoethyl 4-benzylphenyl ether, 2-bromoethyl 4-acetamidophenyl ether, 3-bromopropyl phenyl ether, 3-

bromopropyl 4-tert-butylphenyl ether, 3-bromopropyl 2,6-dimethylphenyl ether or 3-bromopropyl 2,6-dibromo-4-thiocyanatophenyl ether.

2,6-dimethylmorpholinocarboxylic esters of the formula IV are, for example, C_1-C_{20}-alkyl 2,6-dimethylmorpholino-acetate, phenyl 2,6-dimethylmorpholinoacetate, phenyl 2,6-dimethylmorpholinothioacetate, 4-chlorophenyl 2,6-dimethylmorpholinoacetate, 4-nitrophenyl 2,6-dimethylmorpholinoacetate, 3,4-dichlorophenyl 2,6-dimethylmorpholinoacetate, 2,6-dibromo-4-cyanophenyl 2,6-dimethylmorpholinoacetate, benzyl 2,6-dimethylmorpholinoacetate, 2,6-dichlorobenzyl 2,6-dimethylmorpholinoacetate, methyl 2,6-dimethylmorpholino-2-propionate, methyl 2,6-dimethylmorpholino-2-butyrate or, if R^3 is absent, the acetate.

2,6-Dimethylmorpholino alkylphenyl ethers of the formula IV are, for example, 2-(2,6-dimethylmorpholino)ethyl phenyl ether, 2-(2,6-dimethylmorpholino)ethyl 4-cyanophenyl ether, 2-(2,6-dimethylmorpholino)ethyl 4-tert-butylphenyl ether, 2-(2,6-dimethylmorpholino)ethyl 4-nitrophenyl ether, 2-(2,6-dimethylmorpholino)ethyl 3,4-dichlorophenyl ether, 2-(2,6-dimethylmorpholino)ethyl 2,6-dichloro-4-cyanatophenyl ether, 3-(2,6-dimethylmorpholino)propyl phenyl ether, 3-(2,6-dimethylmorpholino)propyl 4-tert-butylphenyl ether, 3-(2,6-dimethylmorpholino)propyl 3,5-dichlorophenyl ether, 3-(2,6-dimethylmorpholino)propyl 2,6-dimethylphenyl ether or 3-(2,6-dimethylmorpholino)propyl 2,6-dibromo-4-thiocyanatophenyl ether.

Alkyl halides of the formula V are, for example, n-decyl chloride, n-dodecyl chloride, n-tridecyl chloride, iso-tridecyl chloride, 1,5,9-trimethyldecyl chloride, pentadecyl bromide or didecyl bromide.

The starting compounds for the preparation of the compounds according to the invention are known per se or can be prepared by processes known per se.

The reaction to give the compounds of the formula I according to the invention are, if appropriate, carried out in the presence of a solvent or diluent at a temperature in the range of between 10 and 180°C, preferably between 30 and 150°C. The starting substances of the formula II or of the formula IV are reacted in stoichiometric amounts with a compound of the formula III or of the formula V or preferably with an excess of 10 to 100% of a compound of the formula III or of the formula V beyond the stoichiometric amount, based on the starting materials of the formula II or of the formula IV.

Preferred solvents or diluents which can be employed are, for example, aliphatic or aromatic, optionally halogenated hydrocarbons such as n-pentane, cyclohexane, benzene, toluene, chlorobenzene, chloroform or methylene chloride; aliphatic ketones such as acetone, methyl ethyl ketone or cyclohexanone; ethers such as diethyl ether, tetrahydrofuran or dioxane; alcohols such as methanol, ethanol, propanols, butanols or hexanols; nitriles such as acetonitrile; esters, such as methyl acetate; amides such as dimethylformamide, dimethylacetamide or N-methyl-pyrrolidone; dimethyl sulphoxide or water, or mixtures of these solvents.

The isolation of the compounds of the general formula I according to the invention from the reaction mixtures is not absolutely necessary since they can also be employed for making fungicidal preparations without further purification operation.

The active compounds of the general formula I according to the invention have a potent activity against

microorganisms and can accordingly be used for combating fungal pathogens in agriculture and in horticulture. Using the active compounds, it is possible to combat undesired fungi which are found on plants or plant parts. The active compounds of the general formula I are furthermore suitable as seed-dressing compositions for the treatment of seed and planting material as a protection from fungal infections and can be employed against soil-borne phytopathogenic fungi. In addition, the active compounds, where employed, have a positive effect on the growth processes of crop plants.

The starting compounds for the preparation of the compounds according to the invention are known per se or can be prepared by methods known per se.

The active compounds according to the invention are particularly suitable for preventing and curing plant diseases which are caused by fungus, such as, for example, Erysiphe graminis (powdery mildew of cereals) Erysiphe cichoracearum (powdery mildew of cucurbits), Erysiphe polygoni (powdery mildew of bean), Podosphaera leucotricha (apple mildew), Sphaerotheca pannosa (powdery mildew of rose), Uncinula necator (powdery mildew of grapevine); rust diseases, such as those of the genera Puccinia, Uromyces or Hemileia, in particular Puccinia graminis (stem rust of cereals), Puccinia coronata (crown rust of oats), Puccinis sorghi (maize rust), Puccinia recondita (leaf rust of cereals), Uromyces fabae (bean rust), Hemileia vastatrix (coffee leaf rust); Botrytis cinerea on grapevines and strawberries; Monilia fructigena on apples; Plasmopara viticola on grapevines; Mycosphaerella musicola on bananas; Corticum salmonicolor on Hevea; Ganoderma pseudoferreum on Hevea; Exobasidium vexans on tea; Phytophtora infestans on potatoes and tomatoes; Alternaria solani on tomatoes. Furthermore, various of these active

substances also have different activity against phytopathogenic fungi such as, for example, Ustilago avenae (loose smut of oats), Ophiobolus graminis (foot rot of cereals), Septoria nodorum (leaf spot and glume blotch of cereals), Venturia inaequalis (apple scab) and further fungal pathogens such as Rhizoctonia, tilletia, Helminthosporium, Peronospora, Pythium, Alternaria, Mucor, Sclerotinia, Fusarium, Pseudocercosporella and Cladosporium.

Of particular interest are the active compounds according to the invention for combating a multiplicity of fungal diseases on a variety of crop plants or their seeds, in particular wheat, rye, barley, oats, rice, maize, cotton, soya, coffee, bananas, sugar cane, fruit, ornamentals in horticulture, vegetables such as cucumbers, beans or cucurbits.

In addition, the active compounds according to the invention can have a positive desired effect on the development of crop plants as a result of their plant-growth-regulatory properties. The effects of the compounds depend essentially on the timing of the application based on the developmental stage of the seed or the plants, on the application rates applied to the plants or their environment, and on the type of application.

Moreover, the active compounds also afford good activity against wood-discolouring and wood-destroying fungi such as, for example, Pullaria pullulans, Aspergillus niger, Polystictus versicolor or Chaetomium globosum.

Furthermore, the active compounds of the general formula I according to the invention display good activity against moulds such as, for example, Penicillium, Fusarium or Aspergillus species, which bring about a deterioration of agricultural products

with a high water content or processed products of agricultural produce during storage or intermediate storage. Products to be treated in this manner comprise, for example, apples, oranges, tangerines, lemons, grapefruits, peanuts, cereals and cereal products or pulses and ground pulses.

In addition to having a broad fungicidal spectrum of activity, the active compounds according to the invention also display various activities against phytopathogenic bacteria such as, for example, Xanthomonas or Erwinia species.

Some of the active compounds are also active against fungi which are pathogenic for humans, such as, for example, Trichophyton and Candida species.

Some of the active compounds of the general formula I are distinguished by a systemic activity, in addition to the protective activity. Thus, they are taken up both via the root and via the leaves and are translocated in the plant tissue or supplied to the aerial parts of the plants via the seed.

The active compounds according to the invention are furthermore suitable for controlling resistant strains of fungal pathogens which display symptoms of resistance to known fungicidal active compounds, such as, for example, active compounds from the group of the dicarboximide fungicides, such as, for example 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine (vinclozolin) or 5-methyl-5-methoxymethyl-3-(3,5-dichlorophenyl)-1,3-oxazolidine-2,4-dione (myclozolin); active compounds from the group of the benzimidazole or thiophanate fungicides such as, for example, methyl 1-(n-butylcarbamoyl)-benzimidazol-2-ylcarbamate (benomyl), methyl benzimidazol-2-ylcarbamate (carbendazim) or 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene (thiophanate); active compounds

from the group of the azole fungicides such as, for example, 1-(4-chlorophenoxy-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-one (triadimefon) or 1-[2'-(2",4"-dichlorophenyl)-2'-(propenyloxy)ethyl]-1,3-imidazole (imazalil); active compounds from the group of the fungicides containing aromatic hydrocarbons such as, for example, 2,5-dichloro-1,4-dimethoxybenzene (chloroneb) or 2,6-dichloro-4-nitroaniline (dichloran); active compounds from the group of the acylalanine fungicides such as, for example, methyl DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)alaninate (metalaxyl) or methyl DL-N-(2,6-dimethylphenyl)-N-(2-furoyl)alaninate (furalaxyl), or active compounds from the group of the pyrimidine fungicides such as, for example, 5-butyl-2-dimethylamino-4-hydroxy-6-methyl-pyrimidine (dimethirimol) or 2-chlorophenyl-4-chloro-phenylpyrimidin-5-ylmethanol (fenarimol).

The anions X^- shown in the general formula I of the active compounds according to the invention are not critical for the fungicidal activity.

The active compounds according to the invention can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusts, foams, pastes, soluble powders, granules, natural and synthetic materials impregnated with active compound, and microencapsulations in polymeric substances, and in coating compositions for seeds and in ULV cold- and hot-fogging formulations.

These formulations are produced in a known manner, for example by mixing or grinding the active compounds of the general formula I according to the invention with solvents and/or carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants.

Liquid solvents which are suitable are: aromatics such as toluene, xylene, or alkylnaphthalenes; chlorinated

aromatics and chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride; aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions; alcohols such as butanols or glycols as well as their esters and ethers; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone; strongly polar solvents such as water, dimethylformamide and dimethyl sulphoxide. Likewise liquefied solvents which are gaseous under standard conditions, such as, for example aerosol propellants, such as halohydrocarbons, propane, butane, nitrogen and carbon dioxide, may be employed.

Suitable solid carriers are, for example, ground natural minerals such as kaolins, clays, talc, chalk, quartz, montmorillonite or diatomaceous earth, and ground synthetic minerals such as highly disperse silica, alumina and silicates. Solid carriers for granules which can be used are, for example, crushed and fractionated natural rocks such as calcite, marble, pumice and dolomite, and synthetic granules of inorganic or organic meals, and granules of organic materials such as sawdust, cellulose powder, tree bark meal, and nutshell meal.

Emulsifiers which can be used are, for example, nonionic and anionic emulsifiers such as alkali metal salts, alkaline earth metal salts or ammonium salts of ligninosulphonic acid, naphthalenesulphonic acids, phenolsulphonic acids, alkylarylsulphonates, alkyl sulphates, alkylsulphonates, alkali metal salts and alkaline earth metal salts of dibutylnaphthalenesulphonic acid, lauryl ether sulphate, fatty alcohol sulphates, alkali metal salts and alkaline earth metal salts of fatty acids, salts of sulphated hexadecanols, heptadecanols or octadecanols, salts of sulphated fatty alcohol glycol ethers, condensates of sulphonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene, or of the naphthalenesulphonic acids, with phenol and formaldehyde, polyoxyethylene octylphenol

ether, alkylphenol polyglycol ether, tributylphenyl polyglycol ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal and sorbitol esters.
Suitable dispersants are, for example, lignin-sulphite waste liquors and methylcellulose.
Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of latices such as gum arabic, polyvinyl alcohol and polyvinyl acetate, may be used in the formulations.

Further additives which may be present in the formulations of the active compounds may be colorants and trace nutrients.

In general, the formulations contain between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90% by weight.

The method according to the invention for controlling fungi is characterized in that an effective amount of fungicidal compositions containing the active compounds of the general formula I according to the invention are allowed to act on fungi or on the objects to be protected from fungal attack.

In the formulations or in the various use forms, the active compounds according to the invention can be mixed, and applied together, with other known active compounds such as fungicides, bactericides, insecticides, acaricides, nematicides, herbicides, growth regulators, plant nutrients and soil conditioners. In many cases, a mixture with fungicides results in a widening of the fungicidal spectrum of action. In a number of mixtures of the active compounds according to the invention with known fungicides, synergistic effects may also be found; here, the

fungicidal activity of the combined product exceeds that of the sum of the activities of the individual components.

Fungicides which can be combined with the active compounds according to the invention, without limiting the possible combinations, are, for example:

sulphur,

dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate and zinc ethylenebisdithiocarbamate,

tetramethylthiuram sulphides,

ammonia complex of zinc (N,N-ethylenebisdithiocarbamate) and N,N'-polyethylenebis(thiocarbamoyl)disulphide,

ammonia complex of zinc (N,N'-propylenebisdithiocarbamate) and N,N'-propylenebis(thiocarbamoyl) disulphide,

N-trichloromethylthiotetrahydrophthalimide,

N-trichloromethylthiophthalimide,

N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide,

4,6-dinitro-2-(1-(methylheptyl)phenyl crotonate,

4,6-dinitro-2-sec-butylphenyl 3,3-dimethylacrylate,

4,6-dinitro-2-sec-butylphenyl isopropylcarbonate,

methyl 1-(n-butylcarbamoyl)benzimidazol-2-ylcarbamate,

methyl benzimidazol-2-ylcarbamate,

2-(fur-2-yl)benzimidazole,

2-(thiazol-4-yl)benzimidazole,

1,2-bis(3-methoxycarbonyl-2-thioureido)benzene,

1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene,

2,3-dihydro-6-methyl-5-phenylcarbamoyl-1,4-oxathiine,

2,3-dihydro-6-methyl-5-phenylcarbamoyl-1,4-oxathiine 4,4-dioxide,

tetrachloroisophthalonitrile,

2,3-dichloro-1,4-napthoquinone,

2,3-dicyano-1,4-dithioanthraquinone,

N-tridecyl-2,6-dimethylmorpholine and its salts,

N-C_{10}-C_{14}-alkyl-2,5- and/or 2,6-dimethylmorpholine,

N-cyclododecyl-2,6-dimethylmorpholine and its salts,
N-[3-p-tert-butylphenyl)-2-methylpropyl]-2,6-cis-dimethylmorpholine and its salts,
N,N'-bis(1-formamido-2,2,2-trichloroethyl)piperazine
N-(1-formamido-2,2,2-trichloroethyl)-3,4-dichloro-aniline,
N-(1-formamido-2,2,2-trichloroethyl)morpholine,
5-butyl-2-ethylamino-4-hydroxy-6-methylpyrimidine,
5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine,
2,4-dichlorophenylphenylpyrimidin-5ylmethanol,
2-chlorophenyl-4-chlorophenylpyrimidin-5-ylmethanol,
bis(4-chlorophenyl)pyridin-3-ylmethanol,
5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-1,3-oxazolidine 2,4-dione,
5-methyl-5-methoxymethyl-3-(3,5-dichlorophenyl)-1,3-oxazolidine-2,4-dione,
3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxo-imidazolidine-1-carboxamide,
N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide,
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-one
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-ol
1-[2-(2,4-dichlorophenyl)-2-(propenyloxy)ethyl]-imidazole
1-[N-propyl-N-(2,4,6-trichlorophenoxy)ethyl-carbamoyl]imidazole
1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole
1-[2-(2,4-dichlorophenyl)4-n-propyl-1,3-dioxolan-2yl-methyl]-1H-1,2,4-triazole
1-(2,4-dichlorophenyl)-2-(1,2,4-triazol-1-yl)-4,4-dimethylpentan-3-one
2,5-dichloro-1,4-dimethoxybenzene
2,6-dichloro-4-nitroaniline
diphenyl
2-methylbenzoanilide
2-iodobenzoanilide

2,5-dimethylfuran-3-carboxanilide
2,4,5-trimethylfuran-3-carboxanilide
N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide
3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]-glutarimide
N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulphodiamide
methyl DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alaninate
methyl DL-N-(2,6-dimethylphenyl)-N-(2-furoyl)alaninate
N-(2,6-dimethylphenyl)-N-chloroacetyl-DL-2-amino-butyrolactone
2,4-dichloro-6-(2-chloroanilino)-s-triazine
O,O-diethyl phthalimidophosphonothioate
5-amino-1-(bis(dimethylamino)phosphinyl)-3-phenyl-1,2,4-triazole
O,O-diethyl S-benzyl thiophosphate
2-thio-1,3-dithio(4,5-b)quinoxaline
4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone
pyridine-2-thiol 1-oxide,
8-hydroxyquinoline and its salts,
sodium 4-dimethylaminophenyldiazosulfonate
diisopropyl 5-nitroisophthalate
2-cyano-N-(ethylaminocarbonyl)-2-(methoxyimino)-acetamide
2-heptadecyl-2-imidazoline acetate
dodecylguanidine acetate

The active compounds as such, in the form of their formulations or in the use forms prepared therefrom by further dilution, can be applied in the usual manner, for example by pouring, dipping, spraying, atomizing, fogging, injecting, slurrying, brushing on, dusting, scattering, dry seed treatment, solvent-based liquid treatment, water-based liquid treatment, slurry treatment or incrusting.

In the treatment of plant parts, the active compound concentrations in the use forms can be varied within a

substantial range. They are, in general, between 0.0001 and 1% by weight, preferably between 0.5 and 0.01% by weight. The application rates of active compound depend on the specific purpose and are generally between 0.1 and 3 kg of active compound per hectare.

In the treatment of seed, active compound quantities of from 0.001 to 50 g or more are generally required per kilogram of seed, preferably from 0.01 to 10 g.

For the conservation or post-harvest-treatment of agricultural commodities or processed agricultural products, the active compound quantities required are from 0.01 to 100 g per kilogram of product to be treated, preferably from 0.1 to 50 g.

Active compound concentrations of from 0.0001 to 0.1% by weight, preferably from 0.001 to 0.05% by weight, are required at the site of action when treating the soil.

Without imposing any limitation, the examples which follow are intended to illustrate the invention in greater detail and to demonstrate the activity of the compounds of the general formula I according to the invention.

Examples

The examples which follow illustrate the preparation of the compounds according to the invention.

Example 1

Methyl N-isotridecyl-2,6-dimethylmorpholinio-acetate chloride

30 g of N-isotridecyl-2,6-dimethylmorpholine and 10.9 g of methyl chloroacetate are refluxed for 20 hours in 100 ml of acetonitrile with addition of a catalytic amount of sodium iodide. The mixture is cooled and the solvent is distilled off in vacuo. The product is triturated in n-hexane. After concentration in vacuo,

38 g of a yellowish-brown viscous oil are obtained (compound No. 5).

IR spectrum (film: C = O - absorption 1740 cm^{-1}.

Example 2

3,4-Dichlorophenyl N-isotridecyl-2,6-dimethyl-morpholinio-acetate chloride

30 g of N-isotridecyl-2,6-dimethylmorpholine and 24 g of 3,4-dichlorophenyl chloroacetate are refluxed for 16 hours in 100 ml of n-butanol with addition of a catalytic amount of sodium iodide. The mixture is cooled and the solvent is distilled off in vacuo. The product which remains is dissolved in a little diethyl ether and treated with n-hexane until its separation as oily phase is complete. After concentration in vacuo, 48 g of a dark brown resin are obtained (compound No. 55).

IR spectrum (film): C = O - absorption 1740 cm^{-1}

C = C - absorption (aromatic) 1590 cm^{-1}

Example 3

Methyl 2-(N-isotridecyl-2,6-dimethyl-morpholinio)propionate chloride

20 g of methyl 2-(2,6-dimethylmorpholino)propionate and 22 g of iso-tridecyl chloride (mixture of different C_{11}-C_{14}-alkyl chlorides containing 60 to 70% of n-tridecyl chloride) in 100 ml of dimethylformamide are refluxed for 10 hours. After cooling, the solvent is distilled off in vacuo. The product is dissolved in a little acetone and treated with n-hexane until its separation as oily phase is complete. Concentration in vacuo gives 19 g of a pale brown resin (compound No. 8).

IR spectrum (film): C = O - absorption 1735 cm^{-1}

Example 4

3-(N-iso-Tridecyl-2,6-dimethylmorpholinio)propyl 2,6-dimethylphenyl ether bromide

15 g of N-iso-tridecyl-2,6-dimethylmorpholine and 12.2 g of 3-bromopropyl 2,6-dimethylphenyl ether in 50 ml of acetonitrile are refluxed for 23 hours with addition of a catalytic amount of sodium iodide. After cooling, the solvent is distilled off in vacuo. The residue is taken up in a little acetone and the solution is treated with n-hexane until separation is complete. The oily phase is separated off and freed from residue solvent in vacuo. This gives 21 g of a yellowish-brown viscose oil (compound No. 107).

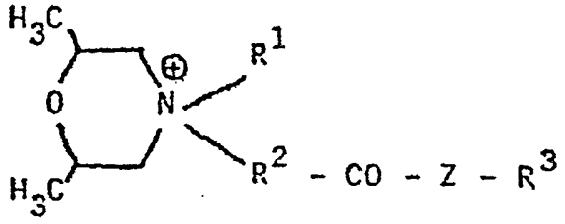
Example 5

2-(N-iso-Tridecyl-2,6-dimethylmorpholinio)-ethyl 3,4-dichlorophenyl ether chloride

17 g of 2-(2,6-dimethylmorpholino)-ethyl 3,4-dichlorophenyl ether and 11 g of iso-tridecyl chloride (mixture of various C_{11}-C_{14}-alkyl halides containing 60 to 70% of n-tridecyl chloride) in 50 ml of dimethylformamide are refluxed for 10 hours. The mixture is allowed to cool and the solvent is distilled off in vacuo. The residue which remains is dissolved in a little acetone and treated with n-hexane until its complete separation as oily phase.

The product is separated off and freed from residual solvent in vacuo. This gives 19 g of a brown resin-like product (compound No. 106).

The compounds of the general formula I listed hereinbelow, which, as a rule, are yellow to brown viscous oils or resins, are readily soluble in polar solvents such as, for example, alcohols, acetone, dimethylformamide and dimethyl sulphoxide and are characterized by IR spectra are prepared analogously.



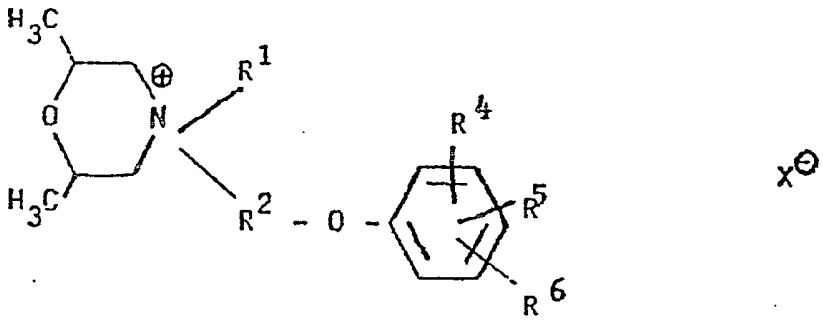
$X^{\ominus}$ (I)

No.	R^1	R^2	Z	R^3	X
1	n-decyl	CH_2	O	methyl	Cl
2	n-dodecyl	CH_2	O	methyl	Cl
3	n-tridecyl	CH_2	O	methyl	Cl
4	1,5,9-trimethyldecyl	CH_2	O	methyl	Cl
5	iso-tridecyl	CH_2	O	methyl	Cl
6	n-pentadecyl	CH_2	O	methyl	Br
7	n-didecyl	CH_2	O	methyl	Br
8	iso-tridecyl	$CH(CH_3)$	O	methyl	Cl
9	iso-tridecyl	$CH(C_2H_5)$	O	methyl	Br
10	iso-tridecyl	$C(CH_3)_2$	O	methyl	Br
11	iso-tridecyl	$C(C_2H_5)_2$	O	methyl	Br
12	iso-tridecyl	$CH(C_5H_{11})$	O	methyl	Br
13	iso-tridecyl	$(CH_2)_3$	O	methyl	Cl
14	iso-tridecyl	CH_2	O	n-butyl	Cl
15	iso-tridecyl	CH_2	S	n-butyl	Cl
16	iso-tridecyl	CH_2	O	2-ethylhexyl	Cl
17	iso-tridecyl	CH_2	O	n-dodecyl	Cl
18	iso-tridecyl	CH_2	O	iso-octadecyl	Cl
19	iso-tridecyl	CH_2	O	4-hydroxybutyl	Cl
20	iso-tridecyl	CH_2	O	2-ethoxyethyl	Cl
21	iso-tridecyl	CH_2	O	4-chlorobutyl	Cl
22	iso-tridecyl	CH_2	O	2,2,2-trichloro-ethyl	Cl
23	iso-tridecyl	CH_2	O	2-nitroethyl	Cl
24	iso-tridecyl	CH_2	O	2-cyanoethyl	Cl
25	iso-tridecyl	CH_2	O	cyclopentyl	Cl
26	iso-tridecyl	CH_2	S	cyclohexyl	Cl
27	iso-tridecyl	CH_2	O	2,6-dimethyl-cyclohexyl	Cl

No.	R^1	R^2	Z	R^3	X
28	iso-tridecyl	CH_2	O	cyclooctyl	Cl
29	iso-tridecyl	CH_2	O	cyclododecyl	Cl
30	iso-tridecyl	CH_2	O	5-(2-ethylcyclo-hexyl)pentyl	Cl
31	iso-tridecyl	CH_2	O	cyclododecyl-methyl	Cl
32	iso-tridecyl	CH_2	O	allyl	Cl
33	iso-tridecyl	CH_2	O	crotyl	Cl
34	iso-tridecyl	CH_2	O	propargyl	Cl
35	iso-tridecyl	CH_2	O	phenyl	Cl
36	iso-tridecyl	CH_2	S	phenyl	Cl
37	iso-tridecyl	CH_2	O	1-naphthyl	Cl
38	iso-tridecyl	CH_2	O	4-diphenyl	Cl
39	iso-tridecyl	CH_2	O	2-chlorophenyl	Cl
40	iso-tridecyl	CH_2	O	3-bromophenyl	Cl
41	iso-tridecyl	CH_2	O	4-chlorophenyl	Cl
42	iso-tridecyl	CH_2		4-sec-butyl-phenyl	Cl
43	iso-tridecyl	CH_2	O	4-tert-butyl-phenyl	Cl
44	iso-tridecyl	CH_2	O	2-methoxyphenyl	Cl
45	iso-tridecyl	CH_2	O	4-methoxyphenyl	Cl
46	iso-tridecyl	CH_2	O	4-propionylphenyl	Cl
47	iso-tridecyl	CH_2	O	4-benzylphenyl	Cl
48	iso-tridecyl	CH_2	O	2-nitrophenyl	Cl
49	iso-tridecyl	CH_2	O	4-nitrophenyl	Cl
50	iso-tridecyl	CH_2	O	4-cyanophenyl	Cl
51	iso-tridecyl	CH_2	O	2,3-dichloro-phenyl	Cl
52	iso-tridecyl	CH_2	O	2,4-dichloro-phenyl	Cl
53	iso-tridecyl	CH_2	O	2,5-dichloro-phenyl	Cl
54	iso-tridecyl	CH_2	O	2,6-dichloro-phenyl	Cl
55	iso-tridecyl	CH_2	O	3,4-dichloro-	Cl

No.	R^1	R^2	Z	R^3	X
				phenyl	
56	iso-tridecyl	CH_2	O	3,5-dichloro-phenyl	Cl
57	iso-tridecyl	CH_2	O	2,6-dimethyl-phenyl	Cl
58	iso-tridecyl	CH_2	O	3,4-dimethyl-phenyl	Cl
59	iso-tridecyl	CH_2	O	2,3-dimethoxy-phenyl	Cl
60	iso-tridecyl	CH_2	O	2-chloro-4-nitrophenyl	Cl
61	iso-tridecyl	CH_2	O	2,4,6-trichloro-phenyl	Cl
62	iso-tridecyl	CH_2	O	2,3,5-trichloro-phenyl	Cl
63	iso-tridecyl	CH_2	O	2,3,6-trimethyl-phenyl	Cl
64	iso-tridecyl	CH_2	O	2,6-dibromo-4-nitrophenyl	Cl
65	iso-tridecyl	CH_2	O	2,6-dibromo-4-cyanophenyl	Cl
66	iso-tridecyl	CH_2	O	2,4-dichloro-6-methylphenyl	Cl
67	iso-tridecyl	CH_2	O	benzyl	Cl
68	iso-tridecyl	CH_2	S	benzyl	Cl
69	iso-tridecyl	CH_2	O	4-chlorobenzyl	Cl
70	iso-tridecyl	CH_2	O	4-bromobenzyl	Cl
71	iso-tridecyl	CH_2	O	4-methylbenzyl	Cl
72	iso-tridecyl	CH_2	O	4-tert-butyl-benzyl	Cl
73	iso-tridecyl	CH_2	O	3-methoxybenzyl	Cl
74	iso-tridecyl	CH_2	O	4-nitrobenzyl	Cl
75	iso-tridecyl	CH_2	O	4-cyanobenzyl	Cl
76	iso-tridecyl	CH_2	O	2,4-dichloro-benzyl	Cl
77	iso-tridecyl	CH_2	O	2,6-dichloro-benzyl	Cl

No.	R^1	R^2	Z	R^3	X
78	iso-tridecyl	CH_2	O	2,3,4-trichloro-benzyl	Cl
79	iso-tridecyl	CH_2	O	2,3,6-trichloro-benzyl	Cl
80	iso-tridecyl	CH_2	O	3-phenylpropyl	Cl
81	iso-tridecyl	CH_2-CO-O^-			



$X^{\ominus}$ (I)

No.	R^1	R^2	R^4	R^5	R^6	X
82	n-octyl	$(CH_2)_2$	2-Cl	6-Cl	H	Br
83	n-dodecyl	$(CH_2)_3$	4-Cl	H	H	Br
84	n-tridecyl	$(CH_2)_3$	4-Cl	H	H	Br
85	1,5,9-trimethyl-decyl	$(CH_2)_3$	4-Cl	H	H	Br
86	iso-tridecyl	$(CH_2)_2$	H	H	H	Br
87	iso-tridecyl	$(CH_2)_2$	4-Cl	H	H	Cl
88	iso-tridecyl	$(CH_2)_2$	3-F	H	H	Br
89	iso-tridecyl	$(CH_2)_2$	4-tert-butyl	H	H	Cl
90	iso-tridecyl	$(CH_2)_3$	4-tert-butyl	H	H	Br
91	iso-tridecyl	$(CH_2)_2$	4-OCH_3	H	H	Br
92	iso-tridecyl	$(CH_2)_3$	3-CH_3	H	H	Br
93	iso-tridecyl	$(CH_2)_2$	4-CO-CH_3	H	H	Br
94	iso-tridecyl	$(CH_2)_2$	3-NH-CO-CH_3	H	H	Br
95	iso-tridecyl	$(CH_2)_2$	3-CO-OC_2H_5	H	H	Br
96	iso-tridecyl	$(CH_2)_2$	3-CO-$N(C_2H_5)_2$	H	H	Br

No.	R^1	R^2	R^4	R^5	R^6	X
97	iso-tridecyl	$(CH_2)_2$	4-NO_2	H	H	Br
98	iso-tridecyl	$(CH_2)_2$	4-CN	H	H	Br
99	iso-tridecyl	$(CH_2)_2$	4-phenyl	H	H	Cl
100	iso-tridecyl	$(CH_2)_2$	4-benzyl	H	H	Cl
101	iso-tridecyl	$(CH_2)_2$	2-Br	4-Br	H	Br
102	iso-tridecyl	$(CH_2)_2$	2-Cl	3-Cl	H	Br
103	iso-tridecyl	$(CH_2)_3$	2-Cl	4-Cl	H	Br
104	iso-tridecyl	$(CH_2)_3$	2-Cl	5-Cl	H	Br
105	iso-tridecyl	$(CH_2)_2$	2-Cl	6-Cl	H	Br
106	iso-tridecyl	$(CH_2)_2$	3-Cl	4-Cl	H	Br
107	iso-tridecyl	$(CH_2)_3$	2-CH_3	6-CH_3	H	Br
108	iso-tridecyl	$(CH_2)_2$	3-CH_3	4-CH_3	H	Br
109	iso-tridecyl	$(CH_2)_2$	3-Cl	5-Cl	H	Br
110	iso-tridecyl	$(CH_2)_2$	2-Cl	4-NO_2	H	Br
111	iso-tridecyl	$(CH_2)_2$	2-Cl	4-Cl	6-Cl	Br
112	iso-tridecyl	$(CH_2)_2$	2-CH_3	4-CH_3	6-CH_3	Br
113	iso-tridecyl	$(CH_2)_2$	2-CH_3	4-Cl	6-CH_3	Br
114	iso-tridecyl	$(CH_2)_4$	2-CH_3	4-Cl	6-CH_3	Br
115	iso-tridecyl	$(CH_2)_2$	2-Cl	4-CN	6-Cl	Br
116	iso-tridecyl	$(CH_2)_2$	2-Cl	4-NO_2	6-Cl	Br
117	iso-tridecyl	$(CH_2)_3$	2-Br	4-SCX	6-Br	Br
118	n-$C_{15}H_{31}$	$(CH_2)_2$	4-Cl	H	H	Br
119	n-$C_{20}H_{41}$	$(CH_2)_2$	4-Cl	H	H	Br

Comp. No.	IR spectra of compounds according to the invention (film) [cm^{-1}]
5	2945, 2915, 2860, 1740, 1445, 1390, 1360, 1310, 1195, 1165, 1130, 1100, 1020, 860
8	2955, 2930...2910, 2870, 2680, 2610, 2505, 1735, 1455, 1370, 1325, 1170, 1125, 1080, 1040, 870, 830
14	2970, 2940, 2880, 2450, 1750, 1470, 1385, 1215, 1150, 1120, 1065, 1030, 880
16	2950, 2920, 2865, 1735, 1450, 1365, 1200, 1160, 1070, 1070, 1025, 860
24	2970, 2940, 2885, 2260, 1755, 1470, 1390, 1220, 1180, 890, 850
35	2950, 2925, 2865, 1735, 1595, 1585, 1490, 1460,

	1370, 1260, 1215, 870
41	2960, 2930, 2875, 1750, 1605, 1595, 1465, 1440, 1385, 1270, 1225, 1095, 1030, 875, 835
49	2960, 2930, 2870, 1745, 1610, 1595, 1510, 1500, 1460, 1380, 1335, 1290, 1230, 1165, 1110, 850, 750, 690, 630
55	2950, 2920, 2365, 1740, 1590, 1565, 1470, 1425, 1375, 1320, 1280, 1210, 1115, 1080, 1015, 900, 850, 810
65	2950, 2920, 2860, 2220, 1735, 1590, 1575, 1560, 1530, 1460, 1370, 1285, 1230, 1190, 1125, 1080, 870
82	2945, 2920, 2850, 2615, 1555, 1440, 1365, 1320, 1235, 1190, 1170, 1100, 1040, 1030, 980, 890, 865, 825
86	2950, 2925, 2870, 2600, 2410, 1595, 1495, 1460, 1380, 1330, 1240, 1175, 1150, 1130, 1080, 1010, 920, 895, 875, 835
87	3020, 2960, 2870, 2600, 2470, 1590, 1495, 1465, 1380, 1215, 1180, 1155, 1135, 1085, 1005, 925, 875, 825
90	2950, 2920, 2860, 2670, 2600, 2485, 1605, 1460, 1365, 1330, 1290, 1245, 1175, 1145, 1130, 1110, 1030, 1050, 1020, 875, 825
98	2945, 2930, 2870, 2610, 2225, 1510, 1460, 1380, 1300, 1255, 1170, 1115, 1085, 1050, 1010, 875, 840
105	2960 2930, 2870, 2610, 1565, 1450, 1375, 1325, 1245, 1175, 1140, 1065, 1045, 990, 905, 870
106	2950, 2920, 2870, 2690, 2680, 2620, 2480, 1590, 1570, 1470, 1385, 1330, 1280, 1225, 1175, 1120, 1085, 1060, 1015, 955, 870, 860, 835, 800
107	2960, 2925, 2870, 2680, 2610, 2490, 1585, 1470, 1380, 1325, 1260, 1195, 1175, 1130, 1085, 1050, 870, 830
113	2955, 2920, 2865, 2680, 2610, 2490, 2225, 1525, 1455, 1375, 1325, 1255, 1175, 1130, 1080, 1020, 870, 830

The compounds of the general formula I according to the invention can be employed for example in the form of the following preparations:

Example I

Solution concentrates: 80 parts by weight of compound 5 are mixed with 20 parts by weight of n-methyl-2-pyrrolidone. This gives a solution which is suitable for use in the form of microdrops.

Example II

Emulsifiable concentrates: 25 parts by weight of compound 55 are mixed with 2.5 parts by weight of epoxidized vegetable oil, 10 parts by weight of an alkylarylsulphonate/fatty alcohol polyglycol ether mixture, 5 parts by weight of dimethylformamide and 57.5 parts by weight of xylene. Emulsions of any desired concentration can be prepared from this concentrate by diluting it with water.

Example III

Wettable powder: 40 parts by weight of compound 65 are mixed thoroughly with 5 parts by weight of the sodium salt of a ligninsulphonic acid from a sulphite waste liquor, 1 part by weight of diisobutylnaphthalene-sulphonic acid sodium salt and 54 parts by weight of silica gel, and the mixture is ground in a suitable mill. This gives a wettable powder which can be diluted with water to give suspensions of any desired concentration.

Example IV

Dust: 5 parts by weight of compound 55 are mixed intimately with 95 parts by weight of finely divided kaolin and the mixture is ground. For use, the dusts can be dusted in this form.

Example V

Granules: 5 parts by weight of compound 57 are mixed with 0.25 part by weight of epichlorohydrin and the mixture is dissolved using 6 parts by weight of acetone. Thereafter, 3.5 parts by weight of polyethylene glycol and 0.25 part by weight of cetyl polyglycol ether are added. The resulting solution is sprayed onto kaolin. Thereafter, the acetone is evaporated in vacuo. This give microgranules which can be employed in this form.

Without imposing any limitation, the examples which follow are intended to illustrate the invention in greater detail and to demonstrate the activity of the compounds of the general formula I:

Example A

Mycelial growth test

The fungicidal activity of the compositions against the test fungi is determined in the customary manner as the inhibition of the radial mycelial growth on malt agar medium (2% malt) in Petri dishes of 9 cm diameter at an incubation temperature of 25°C. To this end, the active compounds are dissolved in dimethylformamide, diluted with water and in this form admixed to the liquid agar so that the desired active compound concentration in the medium is obtained. The DMF content does not exceed 0.5% by volume. After cooling, the plates are inoculated. Depending on the growth rate of the fungi, the plates are evaluated when the controls without added active compound show growth across 70 to 90% of the diameter of the dish. The percentage growth inhibition of the active compounds is calculated (Table A).

Table A: Fungal growth inhibition in the mycelial growth test

Compound No.	Active compound conc.	Growth inhibition in percent: Botrytis cinerea 10 µg/ml	Growth inhibition in percent: Phytophthora cactorum 50 µg/ml
Oxycarboxin (known)		20	50
5		88	85
8		91	48
9		92	51
14		89	100
16		79	100
24		91	
35		78	67
41		86	100
49		84	60
55		97	100
57		94	100
64		92	100
65		95	100
81		78	
82		22	
86		90	
87		87	
90		85	
98		86	100
105		83	81
106		88	
107		80	
125		92	100

Example B

Powdery mildew of barley test (Erysiphe graminis/barley)

In tubes filled with sand, barley plants cv. "Astacus" in the one-leaf-stage are sprayed until dew-moist with active compound preparations which are prepared from 1 part by weight of active compound, 100 parts by weight of dimethylformamide and 0.25 part by weight of alkylaryl polyglycol ether and which are diluted with water to the desired active compound concentration. After the spray coating has dried on, the plants are dusted with conidia of powdery mildew of barley (Erysiphe graminis var. hordei). Thereafter, the test plants are placed for a period of 2 to 3 hours into an incubation cabinet at a relative atmospheric humidity of 90 to 100% and thereafter in a greenhouse at temperatures between 20 and 22°C and a relative atmospheric humidity of 75 to 80%. The mildew infestation of the barley plants is determined after 7 days. The score values obtained according to the Stephan system (Arch. Phytopath., Pfl.-schutz 14 (1978), 163-175) are converted into the disease level of Krüger's system (Nachr.-Bl. Pflanzenschutz DDR 1981, 145-147). These data are used to calculate the ABBOTT efficiency using the formula

$$\text{EFF (in \%)} = \frac{\text{diseaselevel(control)} - \text{diseaselevel(variant)}}{\text{diseaselevel(control)}} \times 100$$

The results can be seen from Table B.

Table B: Activity against Erysiphe graminis on barley
Active compound concentration: 10 mg/l

Compound No.	Efficiency in percent
N-Methyl-N-tridecyl-2,6-dimethyl-morpholine methosulphate (disclosed in DE-PS 11 67 588)	82
Triforine (known)	86
5	88
8	82
9	87
14	93
24	97
35	94
55	88
65	90
5	96
24	92
25	93
26	95
34	97

Example C

Powdery mildew of wheat test (Erysiphe graminis/wheat)

Pot-grown wheat plants cv. "Alcedo" in the one-leaf-stage are sprayed until dew-moist with active compound preparations which are prepared from 1 part by weight of active compound, 100 parts by weight of dimethylformamide and 0.25 part by weight of alkylaryl polyglycol ether and which are diluted with water to the desired active compound concentration. After the spray coating has dried on, the plants are dusted with conidia (spores) of powdery mildew of wheat (Erysiphe graminis var. tritici). Thereafter, the test plants are placed for a period of 2 to 3 hours into an incubation cabinet at a relative atmospheric humidity of 90 to 100% and thereafter in a greenhouse at temperatures between 20 and 22°C and a relative atmospheric humidity of 75 to 80%.

The mildew infestation of the wheat plants is determined after 5 days.

The efficacy of the compositions is calculated using the method described in Example B.

The results can be seen from Table C.

Table C: Activity against Erysiphe graminis on wheat
Active compound concentration: 100 mg/l

Compound No.	Efficiency in percent
N-Methyl-N-tridecyl-2,6-dimethyl-morpholinium methosulphate (disclosed in DE-PS 11 67 588)	67
5	88

Example D

Cereal rust test (Puccinia recondita/wheat)

Pot-grown wheat plants cv. "Alcedo" in the two-leaf stage are cut back to a length of 12 cm. The secondary leaf of the plants is removed. Then, the wheat plants are sprayed with active compound preparations which are prepared from 20 parts by weight of active compound, 10 parts by weight of polyoxyethylene sorbitan monostearate (Tween 60), 5 parts by weight of polypropylene glycol, 25 parts by weight of cyclohexanone and 40 parts by weight of toluene and diluted with water to the desired active compound concentration. After the spray coating has dried on, the plants are inoculated with spores of leaf rust of wheat (Puccinia recondita) which are applied in the form of a slurry in water with addition of Tween 60. Thereafter, the test plants are placed into a water-vapour-saturated incubation cabinet for a period of 24 hours and thereafter in a greenhouse at temperatures of from 20 to 22°C and a relative atmospheric humidity of 70 to 80%.

The rust infection of the wheat plants is determined after 10 days.

The efficacy of the compositions is calculated using the method described in Example B.

The results can be seen from Table D.

Table D: Activity against Puccinia recondita on wheat
Active compound concentration: 500 mg/l

Compound No.	Efficacy in percent
Triforine (known)	85
105	99
107	98
5	95

Example E

Powdery mildew of cucurbits test (mixed culture of Erysiphe cichorarearum and Sphaerotheca fuliginea/cucumber)

Pot-grown cucumber plants cv. "Eva" in the four-leaf-stage are inoculated with a conidial suspension of a mixed culture of Erysiphe cichoracearum and Sphaerotheca fuliginea. After 4 days, the plants are sprayed until dew-moist with active compound preparations which are prepared from 1 part by weight of active compound, 100 parts by weight of dimethylformamide and 0.25 part by weight of alkylaryl polyglycol ether and diluted with water to the desired active compound concentration. After the spray coating has dried on, the plants are placed in a greenhouse at a temperature of 20°C under relative atmospheric humidity of 70 to 80%. The mildew infection of the cucumber plants is determined after 6 and 9 days. The score values obtained by the system of Bolle (Nachrichtbl. Dt. Pflanzenschutzdienst 16 (1964), 92-94) are converted into the disease level of Krüger's system and these data are used for calculating the Abbot efficiency.

The results can be seen from Table E.

Table E: Activity against Erysiphe cichoracearum and Sphaerotheca fuliginea (mixed culture) on cucumbers

Active compound concentration: 500 mg/l

Compound No.	Efficiency in percent Days after application of the composition	
	6	9
Tridemorph (known)	100	88
5	100	100

Example F

Botrytis test (Botrytis cinerea/field bean (Vicia faba) pinnule)

Excised pinnules of pot-grown field bean plants (Vicia faba) cv. "Fribo" in the four-leaf stage are brushed with active compound preparations which are prepared from 1 part by weight of active compound, 100 parts by weight of dimethylformamide and 0.25 part by weight of alkylaryl polyglycol ether and diluted with water to the desired active compound concentration. After the spray coating has dried on, the leaves are inoculated with a conidial suspension of Botrytis cinerea which is obtained by rinsing off 12- to 16-day old fungal cultures on malt agar medium (2% malt). The field-bean pinnules are kept in dishes in an incubation cabinet at a temperature of 22°C under relative atmospheric humidity of 90 to 100%.

After 4 days, the Botrytis infection of the field-bean pinnules is determined. The percentage infection based on all of the leaf area is converted into the Abbot efficacy of the compositions.

The results can be seen from Table F.

Table F: Activity against Botrytis cinerea on field bean (Vicia faba) pinnules

Active compound concentration: 100 mg/l

Compound No.	Efficiency in percent
Tridemorph (known)	42
5	45
14	68
55	48
105	62
106	47
107	51

Example G

Phytophthora test (Phythophthora infestans/tomato)

Pot-grown tomato plants cv. "Tamina" in the three-leaf-stage are sprayed to dew point with active compound preparations which are prepared from 1 part by weight of active compound, 100 parts by weight of dimethylformamide and 0.25 part by weight of alkylaryl polyglycol ether and diluted with water to give the desired active compound concentration. After the spray coating has dried on, the tomato plants are inoculated with an aqueous zoospore suspension of Phythophthora infestans. Thereafter, the test plants are placed into an incubation cabinet at temperatures of between 18 and 20°C and a relative atmospheric humidity of 95 to 100%. The Phythophthora infection of the tomato plants is determined after 5 days. The scores obtained are converted into the disease level and the efficacy of the compositions as described in Example B.

The results are shown in Table G.

Table G: Activity against Phythophthora infestans on tomatoes

Compound No.	Active compound concentration in mg/l	efficiency in percent
Zineb (known)	100	57
	200	61
105	100	66
	200	79

Example H

Plant growth regulation test

Cucumber plants cv. "Eva" are grown in the greenhouse to a height of 9 cm in pots in rich humus compost. Ten plants are used for each test variant. The cucumber plants are sprayed with active compound preparations which are prepared from 1 part by weight of active compound, 100 parts by weight of dimethylformamide and 0.25 part by weight of alkylaryl polyglycol ether and diluted with water to the desired active compound concentration.

After a growth period of 14 days after the compositions have been applied, longitudinal measurements are carried out on the treated plants and the untreated control plants.

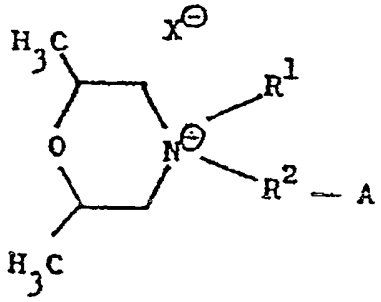
The results can be seen from Table H.

Table H: Effect of foliar treatment on the longitudinal growth of cucumber plants
Active compound concentration: 1000 mg/l

Compound No.	Plant height in cm	Plant height relative
untreated control	23	100
5	15.6	68
105	15	65

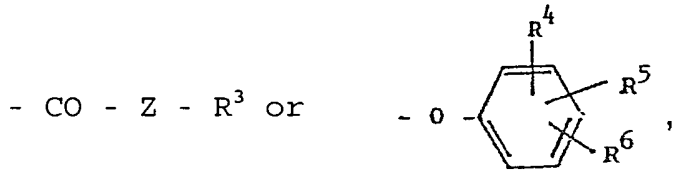
Patent Claims

1. N-Alkyl-2,6-dimethylmorpholiniocarboxylic ester salt and N-alkyl-2,6-dimethylmorpholinio alkylphenyl ether salt of the general formula I,



(I),

wherein A represents the group



in which

R^1 represents straight-chain or branched alkyl having 6 to 20 C atoms,

R^2 represents straight-chain or branched alkylene having 1 to 6 C atoms,

R^3 represents straight-chain or branched alkyl having 1 to 20 C atoms,
a straight-chain or branched alkyl which has 1 to 6 C atoms and which is substituted by halogen, hydroxyl, alkoxy having 1 to 4 C atoms, dialkylamino having 2 to 16 C atoms, nitro and/or cyano,
an alkenyl which has 2 to 6 C atoms and which is optionally substituted by halogen,
alkynyl having 3 to 6 C atoms,
cycloalkyl having 3 to 12 carbon atoms, it being possible for the cycloalkyl radical

optionally to be substituted by one or more alkyl radicals having 1 to 7 C atoms,
cycloalkylalkyl having 4 to 10 C atoms,
aryl which can be monosubstituted or polysubstituted by identical or different substituents from the series consisting of straight-chain or branched alkyl having 1 to 6 C atoms, alkoxy having 1 to 4 C atoms, aryl-lower-alkyl having 7 to 12 C atoms, acyl having 1 to 4 C atoms, halogen, aryl, nitro and/or cyano,
aryl-lower-alkyl which has 7 to 12 C atoms and which can be monosubstituted or polysubstituted by identical or different substituents from the series consisting of straight-chain or branched alkyl having 1 to 6 C atoms, alkoxy having 1 to 4 C atoms, halogen, haloalkyl having 1 to 4 C atoms, nitro and/or cyano,

R^4, R^5 and R^6 independently of one another represent identical or different substituents from the series consisting of hydrogen, straight-chain or branched alkyl having 1 to 6 C atoms, alkoxy having 1 to 4 C atoms, acyl having 1 to 4 C atoms, halogen, haloalkyl having 1 to 4 C atoms, cycloalkyl having 3 to 7 C atoms, aryl-lower-alkyl having 7 to 12 C atoms, aryl, nitro, cyano, thiocyanato, NHCOR', COOR' and/or CONR'R" it being possible for R' and R" independently of one another to represent hydrogen, straight-chain or branched alkyl having 1 to 6 C atoms, aryl or aryl-lower-alkyl having 7 to 12 C atoms,

Z represents oxygen or sulphur and

X^- represents the anion of a nonphytotoxic acid,

or R^3 and X^- are absent.

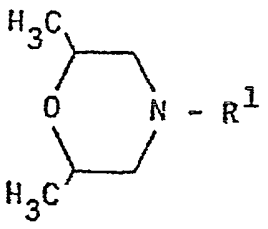
2. Compounds according to Claim 1, characterized in that R^2 is CH_2 or $CH(CH)_3$, R^3 is C_1-C_{14}-alkyl and Z is oxygen.

3. Compounds according to Claim 1, characterized in that R^2 is CH_2, R^3 is halophenyl and Z is oxygen.

4. Compounds according to Claim 1, characterized in that R^2 is CH_2, R^3 is alkylphenyl having 7 to 12 C atoms and Z is oxygen.

5. Process for the preparation of N-alkyl-2,6-dimethylmorpholiniocarboxylic ester salts and N-alkyl-2,6-dimethylmorpholinio alkylphenyl ether salts of the general formula I, characterized in that

a) an N-alkyl-2,6-dimethylmorpholine of the formula II,



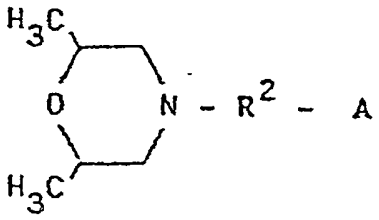
(II)

wherein R^1 has the meaning given in the general formula I
is reacted with a compound of the formula III

$$X - R^2 - A \qquad (III)$$

wherein R^2 and A have the meaning given in the general formula I and X represents halogen,
or,

b) a 2,6-dimethylmorpholinocarboxylic ester or 2,6-dimethylmorpholino alkylphenyl ether of the formula IV,



(IV)

wherein R^2 and A have the meaning given in the general formula I

is reacted with a compound of the formula V,

$$R^1 - X \qquad (V)$$

wherein R^1 has the meaning given in the general formula I and X represents halogen.

6. Fungicidal compositions with additional plant-growth-regulatory activity, containing at least one compound of the general formula I according to Claim 1.

7. Fungicidal compositions with additional plant-growth-regulatory activity, containing at least one compound of the general formula I according to Claim 1 in admixture with inert additives.

8. Method of combating fungi, characterized in that at least one compound of the general formula I according to Claim 1 is allowed to act on fungi or on the objects to be protected from fungal infection.

9. Use of compounds of the general formula I according to Claim 1 for combating fungi and/or for regulating the growth of plants.